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Fate and Transport of Linear Alkylbenzenesulfonate in a Sewage-Contaminated Aquifer: A Comparison of Natural-Gradient Pulsed Tracer Tests

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Two natural-gradient tracer tests were conducted to determine the transport and biodegradation behavior of linear alkylbenzenesulfonate (LAS) surfactant under in situ conditions in a sewage-contaminated aquifer. The tests were conducted in two biogeochemically distinct zones of the aquifer: (1) an aerobic uncontaminated zone (oxic zone) and (2) a moderately aerobic, sewage-contaminated zone (transition zone). Chromatographic separation of the surfactant mixture was observed in both zones and attributed to the retardation of the longer alkyl chain homologues during transport. No significant loss of LAS mass was observed for the oxic zone while 20% of the LAS mass injected into the transition zone was removed due to biodegradation. Biodegradation preferentially removed the longer alkyl chain homologues and the external isomers (i.e., 2- and 3-phenyl). The removal of LAS mass coincided with a decrease in dissolved oxygen concentrations, the appearance of LAS metabolites, and an increase in the number of free-living bacteria with a concomitant change in bacteria morphology. The formation of LAS metabolites accounted for 86% of the LAS mass removed in the transition zone. Over the duration of the test, sorption and biodegradation enriched the LAS mixture in the more water-soluble and biologically resistant components.

Introduction

Linear alkylbenzenesulfonate (LAS) is the highest volume anionic surfactant used in domestic and commercial detergent formulations (*1*). The environmental fate of LAS is of interest because of its widespread use in detergents and subsequent disposal to wastewater treatment facilities. Several reports document the presence of LAS and its biodegradation products in domestic sewage (*2*−*6*). In addition, LAS is persistent under low-oxygen conditions such as those that exist in anaerobic sewage sludge digestors (*3*, *7*). While LAS fate in wastewater treatment systems is well-documented, few studies describe LAS behavior and fate in groundwater (*4, 8*) and how processes such as sorption and biodegradation affect the surfactant mixture composition.

The environmental fate of surfactants in groundwater also is of interest because surfactants are being evaluated as potential agents for enhancing the remediation of aquifers contaminated with dense nonaqueous phase liquids (DNAPL). Numerous laboratory studies describe the ability of surfactants to enhance the solubility and mobility of DNAPLs (*9*−*12*), and several report on the efficiency of surfactant-enhanced DNAPL recovery under field conditions (*13*−*15*). However, none of these studies address surfactant behavior in groundwater per se. Processes such as sorption and biodegradation potentially affect the surfactant mixture composition and thus the physicochemical properties of the mixture such as the critical micelle concentration and the ability to solubilize DNAPL, which are important for predicting the efficiency of surfactant-enhanced DNAPL recovery. In addition, surfactants not completely recovered during remediation have the potential for becoming groundwater contaminants themselves. Therefore, given the potential for surfactants to occur in groundwater, whether as micropollutants or remediation additives, it is important to understand surfactant behavior in subsurface environments.

The U.S. Geological Survey's Cape Cod Toxic Substances Hydrology Research Site is the site of an ongoing investigation of the fate and transport of LAS in sewage-contaminated groundwater. Initially, studies at this site described the occurrence and distribution of LAS and related compounds (*4, 16*). LAS mixtures in oxygen-depleted groundwater with residence times greater than 3 years were depleted in the longer alkyl chain homologues and external isomers (*4*). On the basis of these findings, we hypothesized that LAS persists in groundwater due to oxygen limitation, despite the presence of acclimated indigenous microbial populations. To test the hypothesis, three natural-gradient tracer tests were conducted at the site to characterize quantitatively in situ transport and biodegradation of LAS components in three biogeochemically distinct zones. The first test was conducted in an anaerobic (<0.1 mg/L dissolved oxygen), sewage-contaminated zone (suboxic zone) (*17*). Chromatographic separation of the homologues based on increasing sorption of the longer alkyl chain homologues occurred, but no biodegradation of the mixture was observed during the 45-day test (*17*). In this study, we report the results from tracer tests conducted in an aerobic uncontaminated zone (oxic zone) and a moderately aerobic, sewage-contaminated zone (transition zone) in the same aquifer. These two tests were designed to investigate further the role of dissolved oxygen concentration and indigenous microbial population in LAS biodegradation in groundwater and the effect of sorption and biodegradation processes on the LAS mixture composition observed during transport.

Experimental Section

Site Description. The tracer tests were conducted in an unconfined sand and gravel glacial outwash aquifer at the U.S. Geological Survey's Cape Cod Toxic Waste Research Site near Falmouth, MA (*18, 19*). The aquifer is characterized by an average hydraulic conductivity of 1.3×10^{-3} m/s, a porosity of 0.38, and average porewater velocities that range from 0.3 to 0.5 m/day (*18, 19*). At this location, discharge of secondary sewage effluent to infiltration sand beds from 1936 to 1995 has resulted in a plume of sewage-contaminated groundwater that is ∼5 km long. Numerous studies have

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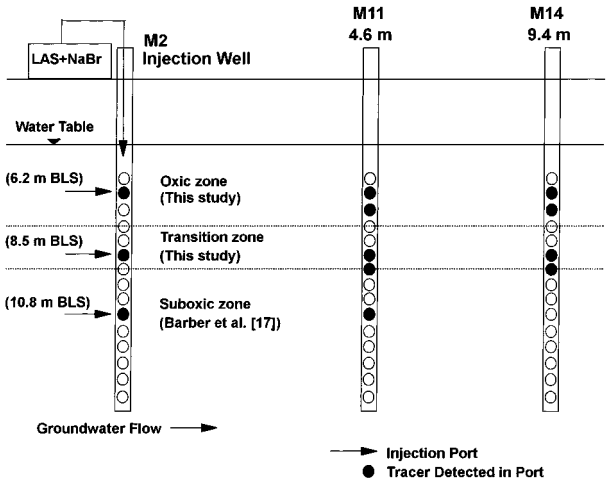

FIGURE 1. Multilevel sampling wells used during the oxic, transition, and suboxic tracer tests including the locations of the injection well (M2), the downgradient monitoring wells M11 and M14, and sampling ports.

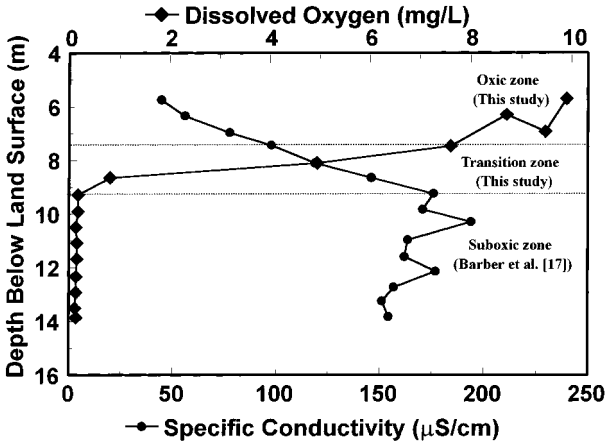

FIGURE 2. Vertical geochemical profile of the aquifer at the injection well (M2) with the oxic, transition, and suboxic zones indicated.

been conducted on the hydrology, microbiology, and contaminant fate and transport in the region of the plume (*19*–*26*).

The tracer tests were conducted 300 m downgradient from the infiltration beds using an array of multilevel monitoring wells, each with 15 discrete sampling ports vertically spaced at 0.6-m intervals (Figure 1). At this location, the aquifer has a vertical geochemical profile (Figure 2) due to uncontaminated groundwater from recharge overlying the contaminant plume (*19*, *20*). There is a ~2 m thick transition zone between the uncontaminated and contaminated groundwater characterized by a sharp increase in specific conductivity and a decrease in dissolved oxygen concentration (Figure 2). The pH increases with depth from approximately pH 5.5 to pH 6.5 over the vertical profile. Background concentrations of LAS were below detection in the oxic zone and were at detection (0.01 mg/L) in the transition zone.

Injections. The tracer tests were conducted in two geochemically distinct zones of the aquifer: (1) oxic zone at 6.2 m below sea level (BLS) with ~8 mg/L dissolved oxygen and (2) the transition zone at 8.5 m BLS with ~1 mg/L dissolved oxygen (Figure 2). The injections in the oxic and transition zones were performed on June 6 and June 7, 1994, respectively. For each injection, a gas-impermeable bag (Aerotech, Ramsey, NJ) was rinsed with groundwater from each zone and then flushed three times with nitrogen gas. Solutions of NaBr (Aldrich Chemical Co., Milwaukee, WI) and a commercial mixture of LAS (Condea Vista, Austin, TX) were prepared in degassed distilled water. The homologue distribution of the LAS mixture was 22% C_{10}, 39% C_{11}, 29% C_{12}, and 9% C_{13}. Approximately 155 L of groundwater from the injection zone was then pumped into the bag with a peristaltic pump fitted with low gas permeability Norprene tubing (Cole-Parmer Instrument Company, Chicago, IL). The oxic zone injectate consisted of a mixture of groundwater pumped from two ports in the injection well, M2, at depths of 6.2 and 6.8 m BLS. The transition zone injectate consisted of a mixture of groundwater pumped from a depth 8.5 m BLS from the injection well (M2) and a second well, M11, located 4.6 m downgradient of M2. In both tests, the bags were kept in a pit filled with groundwater to maintain the temperature of the injectate at the ambient aquifer temperature (~12 °C).

The injectate solutions were injected over a 3-h period at approximately 0.9 L/min. Assuming symmetric initial displacement, each tracer plume would be expected to have a cross-section of 0.92 m. Injectate samples were collected for analysis at the beginning, middle, and end of each injection to verify the initial concentrations of bromide (oxic zone, 95 mg/L; transition zone, 93 mg/L) and LAS (oxic zone, 21.7 mg/L; transition zone, 19.7 mg/L) in the injectate solutions. Dissolved oxygen concentration of the injectate solutions was 6 mg/L for the oxic zone and 0.7 mg/L for the transition zone.

Field Sampling and Analyses. Two monitoring wells located at 4.6 m (M11) and 9.4 m (M14) downgradient from the injection well were monitored during the two tests (Figure 1). Groundwater samples for bromide, LAS, LAS metabolites, and bacteria analysis were collected daily from sampling ports in polyethylene bottles with a peristaltic pump fitted with Norprene tubing. Dissolved oxygen concentrations were determined colorimetrically (CHEMetrics, Calverton, VA) in the discharge line of the peristaltic pump during sample collection. Bromide concentrations were determined on site with an ion-selective electrode and meter (Orion model 250A) after the samples had equilibrated to approximately 25 °C. Semiquantitative LAS concentrations were determined in the field with a colorimetric MBAS (methylene blue active substances) assay (CHEMetrics, Calverton, VA). Quantitative LAS concentrations were determined on samples preserved with 1% v/v formalin by the method of Krueger and Field (*6*). LAS metabolite (i.e., C_4–C_{10} sulfophenylcarboxylates) concentrations were determined on samples preserved with formalin (3% v/v) by the method of Trehy et al. (*27*). Enumerations of total free-living bacteria were determined on samples preserved with formalin (3% v/v) by the method of Harvey et al. (*28*). Frequency of dividing cells (FDC, expressed as the percentage of dividing cells) were obtained during bacterial enumeration by determining the fraction of the total free-living bacterial population with clear invaginations of cell wall between dividing cells by the method of Harvey and George (*29*). Concentrations of Ca^{2+} in groundwater samples were determined by atomic absorption spectrophotometry (Perkin-Elmer 4000). Sediment cores were collected near the well array from depths corresponding to the injection depths in 1.5 m × 5 cm aluminum liners with hollow-stem auger drilling and a wireline-piston core barrel and stored at 4 °C. Sediment organic carbon was determined by the Walkley–Black method on sediment cores collected from the two test zones, and total carbon in sediments was determined by a carbon analyzer (Leco CNS-2000).

Results and Discussion

Tracer Trajectories. Bromide breakthrough curves were constructed by normalizing the observed concentrations to the average injectate concentrations (Figure 3). In both tests, the tracer plume was detected in sampling ports at the injection depth and 0.6 m below the injection depth in each

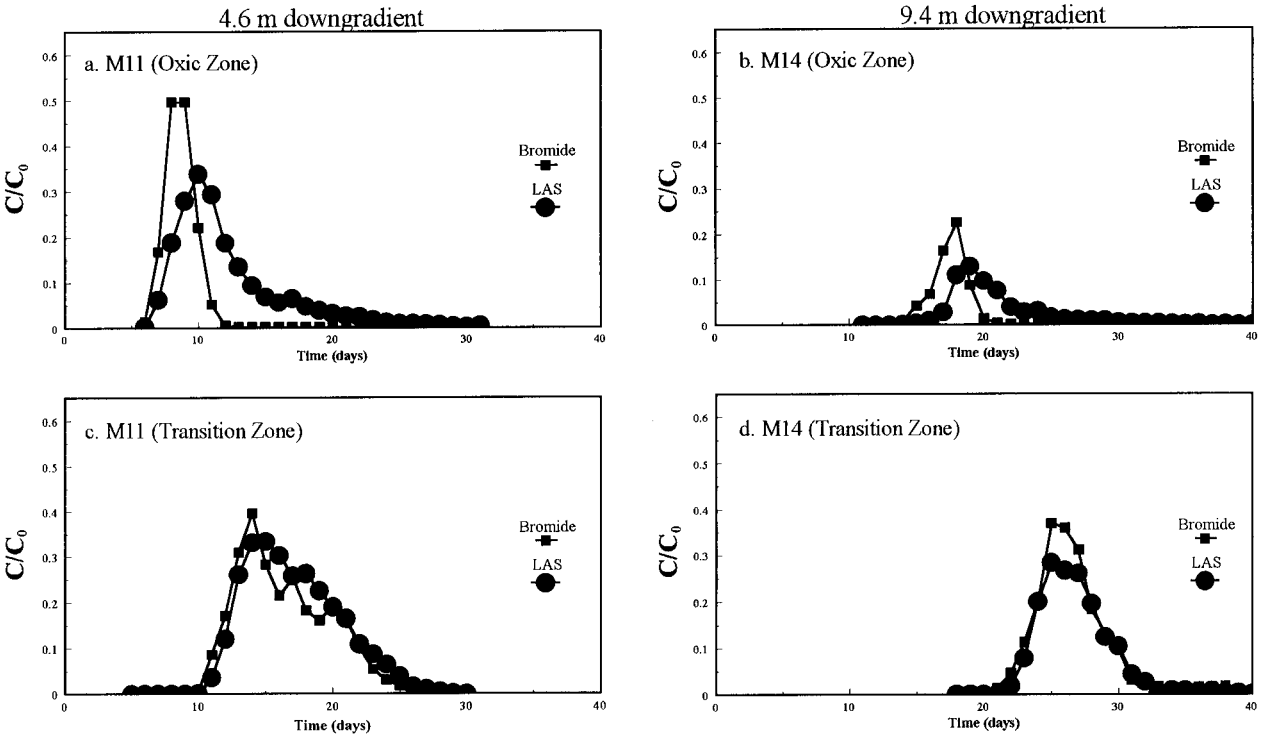

FIGURE 3. Bromide and total LAS breakthrough curves in the oxic zone (a, b) and in the transition zone (c, d) at monitoring wells M11 and M14 located 4.6 and 9.4 m downgradient, respectively.

of the downgradient monitoring wells (Figure 1). The presence of tracer in ports below the injection depth contrasts with the results of the 1993 experiment performed in the suboxic zone in which the tracer was detected only at the injection depth (*17*) (Figure 1). The apparent vertical drop of the tracer plumes could be the result of differences in density between the injectate and groundwater in each zone or the result the presence of more permeable layers underlying the injection zones such that the tracer plume adopted an initial downward trajectory into the more permeable layers. The tracer plumes in both tests passed most directly through sampling ports in wells M11 and M14 at the injection depth, thus the discussion on LAS will focus on data from these wells at 6.2 and 8.5 m BLS.

LAS Transport. LAS breakthrough curves were constructed by normalizing the observed concentrations to the average injectate concentrations (Figure 3). Qualitatively, the bromide and LAS breakthrough curves were nearly coincident in the transition zone, whereas in the oxic zone LAS was retarded relative to bromide and exhibited more tailing. Breakthrough curves of the individual LAS components illustrate that the leading edges are dominated by the shorter alkyl chain homologues and the longer chain homologues dominate the tail, indicating that the mixture separated during transport (Figure 4). Breakthrough curves with multiple peaks observed in well M11 at a depth of 8.5 m BLS (Figures 3c and 4c) may indicate that the tracer plume traveled through a section of aquifer with strata of varying permeabilities (*22, 30*).

Retardation factors, R, were calculated from the average travel times, $\bar{t}$, of the LAS components relative to bromide using the first temporal moment, M_1, of the breakthrough curves (*31, 32*). Estimated retardation factors for total LAS ranged from 1.2 to 1.4 in the oxic zone but were essentially unretarded ($R = 1$) for all sampling ports in the transition zone (Table 1). In both tests, estimated retardation factors increased with increasing alkyl chain length and external substitution, with higher values for the individual LAS components in the oxic zone as compared to the transition zone (Tables 2 and 3). Retardation factors in the transition zone were similar to those obtained in the suboxic zone tracer test for the total LAS mixture ($R = 1.1$) and the 3-phenyl $C_{10}-C_{13}$ homologues ($R = 1.0-1.4$) (*17*). In the oxic zone, sampling was terminated at well M11 before the C_{13} 2- and 3-phenyl isomer concentrations had returned to background levels, resulting in negatively biased retardation estimates for these components. All other homologue concentrations decreased below detection at all monitoring wells during the experiment.

The second temporal moment about the center of mass, M_2, provides a measure of the spread of the tracer plume (*31, 33*). The similarity in second moments for bromide and the LAS components (Tables 2 and 3) indicates that separation of the LAS homologues and isomers during groundwater transport accounts for the apparent tailing observed in the total LAS breakthrough curves. For example, in the oxic zone, the second moment of total LAS (Table 1) was nearly eight times greater than for bromide ($1.3-2.0$ day^2), but there were no significant increases in the second moments of most of the individual LAS components relative to bromide (Table 1). In the transition zone, the similar breakthrough curve shapes (Figure 4b) and second moments of bromide ($10.9-12.0$ day^2) and individual LAS components (Table 3) indicate similar transport behavior for all solutes. Values of M_2 may be unreliable because they are sensitive to solute concentrations in the breakthrough curve tail, which typically are not known accurately (*31, 33*). Thus, values of M_2 were computed using only solute concentrations greater than 1% of the injectate concentration.

The separation of the LAS mixture during transport in both tests is attributed to preferential sorption of LAS components to the aquifer sediments in a manner consistent with a hydrophobic mechanism (*34*). Sediment partition coefficients, K_d (L/kg), were estimated from the retardation factors as previously described (*17*) and varied as a function of alkyl chain length and phenyl position such that sorption increased with increasing hydrophobicity (Figure 5). Estimated values of K_d in both zones increased by a factor of 3.4

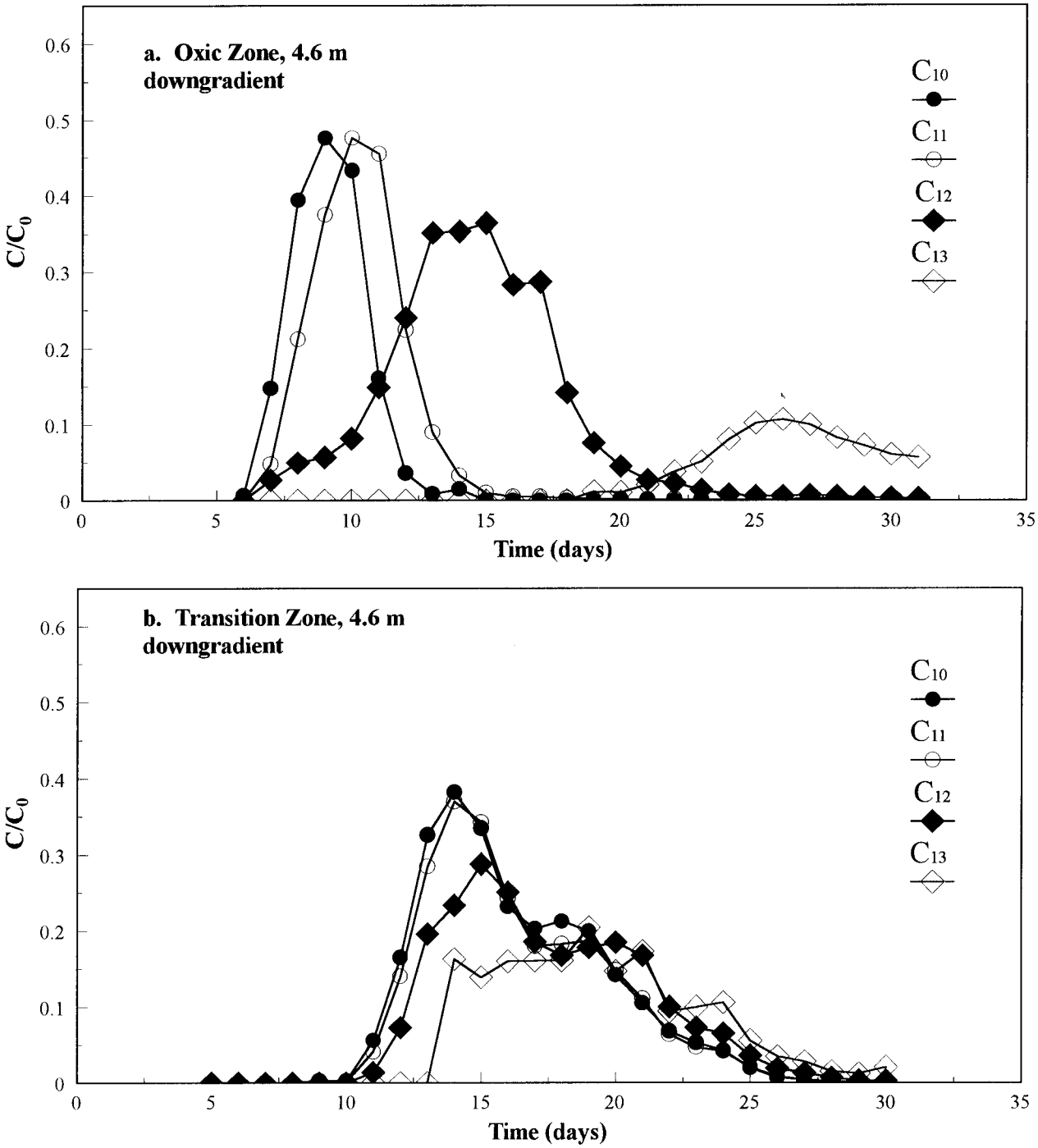

FIGURE 4. Breakthrough curves for the 3-phenyl isomer of the C_{10}−C_{13} LAS homologues in the oxic zone (a) and in the transition zone (b) at well M11 (4.6 m downgradient).

TABLE 1. Breakthrough Curve Results for Total LAS

	monitoring well M11			monitoring well M14		
tracer test	*R*	M_{rel}	M_2 (day^2)	*R*	M_{rel}	M_2 (day^2)
oxic zone	1.4	1.4	18.3	1.2	0.9	13.3
transition zone	1.0	0.9	11.9	1.0	0.8	6.9

(± 0.7) for each additional methylene group and by a factor of 2.8 (± 0.4) between the 5-phenyl and 2-phenyl isomers, which are comparable to the factors of 2.8 and ~2 reported for LAS sorption to river sediments (*34*).

Sorption was greater in the oxic zone with an average increase in log K_d of 0.9 ± 0.1 over the transition zone for the C_{12} and C_{13} homologues based on linear regression results with the relation between LAS sorption and structure being less definite in the transition zone for the least hydrophobic, weakly sorbed LAS components (i.e., C_{10}−C_{11}) (Figure 5). The low degree of sorption indicated by lower K_d values observed in the transition zone is consistent with the low-carbon aquifer sediments at this site. The total sediment carbon content, f_{oc}, was determined to be less than 0.0001 for both the oxic and transition zones. Estimated K_d values for the transition zone at well M11 ranged from 0.003 to 0.086 L/kg for the individual homologues and isomers and 0.010 L/kg for the total mixture and were comparable to values observed in the suboxic zone tracer test (*17*). These K_d values are similar to values of 0.002−0.02 L/kg for the C_{10}−C_{13} LAS

TABLE 2. Breakthrough Curve Results for the Individual LAS Components in the Oxic Zone

	monitoring well M11			monitoring well M14		
LAS component	*R*	M_{rel}	M_2 (day^2)	*R*	M_{rel}	M_2 (day^2)
C_{10} 2-ϕ	1.1	1.2	2.0	1.1	1.0	2.8
C_{10} 3-ϕ	1.0	1.1	1.7	1.0	0.9	2.2
C_{10} 4-ϕ	1.0	1.1	1.6	1.0	0.8	2.3
C_{10} 5-ϕ	1.0	1.1	1.7	1.0	0.8	2.4
C_{11} 2-ϕ	1.3	1.5	4.5	1.2	1.3	4.1
C_{11} 3-ϕ	1.2	1.3	2.8	1.1	1.1	3.0
C_{11} 4-ϕ	1.1	1.2	2.4	1.1	1.0	3.0
C_{11} 5-ϕ	1.1	1.2	2.1	1.1	1.0	3.2
C_{12} 2-ϕ	2.1	1.6	12.7	1.7	0.8	13.0
C_{12} 3-ϕ	1.6	1.8	10.1	1.4	1.2	7.6
C_{12} 4-ϕ	1.5	1.7	6.9	1.3	1.4	6.2
C_{12} 5-ϕ	1.3	1.6	4.8	1.2	1.4	4.4
C_{13} 2-ϕ	2.8	0.2	17.2	nd[a]	nd	nd
C_{13} 3-ϕ	2.9	0.5	8.1	2.4	0.02	0.0
C_{13} 4-ϕ	2.7	1.0	9.9	2.1	0.2	14.7
C_{13} 5-ϕ	2.2	1.7	11.2	1.7	0.7	11.2

[a] nd, not detected.

TABLE 3. Breakthrough Curve Results for the Individual LAS Components in the Transition Zone

	monitoring well M11			monitoring well M14		
LAS component	*R*	M_{rel}	M_2 (day^2)	*R*	M_{rel}	M_2 (day^2)
C_{10} 2-ϕ	1.0	1.0	11.2	1.0	0.9	7.3
C_{10} 3-ϕ	1.0	1.0	10.6	1.0	0.9	6.8
C_{10} 4-ϕ	1.0	1.1	11.4	1.0	1.0	7.7
C_{10} 5-ϕ	1.0	1.1	12.1	1.0	1.1	9.6
C_{11} 2-ϕ	1.0	0.9	11.5	1.0	0.8	6.6
C_{11} 3-ϕ	1.0	0.9	10.6	1.0	0.8	6.4
C_{11} 4-ϕ	1.0	1.0	10.7	1.0	0.9	6.5
C_{11} 5-ϕ	1.0	1.1	11.4	1.0	1.0	8.0
C_{12} 2-ϕ	1.1	0.8	13.8	1.1	0.4	8.3
C_{12} 3-ϕ	1.1	0.9	12.7	1.0	0.7	8.6
C_{12} 4-ϕ	1.0	0.9	11.6	1.0	0.7	8.1
C_{12} 5-ϕ	1.1	1.1	12.5	1.0	1.0	8.7
C_{13} 2-ϕ	1.4	0.2	9.1	nd[a]	nd	nd
C_{13} 3-ϕ	1.2	0.7	13.9	1.1	0.2	9.1
C_{13} 4-ϕ	1.1	0.6	14.6	1.2	0.2	9.3
C_{13} 5-ϕ	1.1	0.9	13.5	1.1	0.4	7.3

[a] nd, not detected.

homologues predicted from the linear free-energy relationship between log K_d and log K_{ow}, assuming an f_{oc} of 0.0001 (*35*), where K_{ow} is the octanol/water partition coefficient. For the C_{10}−C_{13} homologues, log K_{ow} ranges from 1.23 to 2.52 (*34*). However, the K_d values for the oxic zone, which ranged from 0.003 to 0.44 L/kg for individual components and 0.083 L/kg for the total mixture, are significantly greater than K_d values predicted for low-organic carbon sediments and would require an f_{oc} of 0.002 based on the linear free-energy relationship predictions.

Previous studies have reported LAS sorption to be correlated with sediment organic carbon content (*36*−*38*). However, in this and other studies (*34*), LAS sorption did not appear to correlate well with sediment organic carbon content, which leads to consideration of other possible mechanisms. The dominant minerals in the aquifer sediment at this site are quartz and feldspar (*39*), which have negatively charged surfaces that potentially repel the sulfonate group of LAS so that it is weakly sorbed to low-organic carbon sediments at the groundwater pH values (5.5−6.5) measured in this study. During weathering, negatively charged mineral surfaces may develop a positive charge due to the formation of amorphous metal oxide coatings. Such metal oxide coatings composed of iron and aluminum oxyhydroxides typically have pH zero point of charge values of ~7−8 so that they would have positively charged surfaces at pH 5−6 (*39*). At the lower groundwater pH (5.5) of the oxic zone, the positively charged metal oxide coatings may enhance LAS sorption by surface complexation or through electrostatic interactions with the sulfonate group. This effect would not be as pronounced at the higher groundwater pH (6.5) of the transition zone because the sediment surfaces would exhibit less net positive charge. In addition, metal oxide coatings are commonly present in sediments from the oxic zone but typically are not formed under the reducing conditions of the sewage-contaminated transition zone. For example, sediments collected from depths corresponding to the oxic zone had a higher percentage of iron-containing minerals than did sediments from the transition zone (*39*).

Increasing $[H^+]$ and $[Ca^{2+}]$ were reported to increase LAS sorption through electrostatic effects such that $\Delta\log K_d \approx 0.17$ per unit change in pH and $\Delta\log K_d \approx 0.23$ per decade increase in $[Ca^{2+}]$ (*38*). At well M11, $[Ca^{2+}]$ was ~12 times greater in the transition zone (10.8 mg/L) than in the oxic zone (0.9 mg/L). However, the average increase in log K_d of 0.9 ± 0.1 from the transition zone to the oxic zone (Figure 5) is greater than can be accounted for by the increase in either $[H^+]$ or $[Ca^{2+}]$. It is likely that a combination of factors, including hydrophobic and electrostatic interactions, contribute to increased LAS sorption in the oxic zone.

LAS Biodegradation. Relative mass, M_{rel}, which is the value of the zeroeth temporal moment for a given solute normalized to that of the conservative bromide tracer, was used to determine whether the mass of the individual LAS components was conserved ($M_{rel} \cong 1$) or removed ($M_{rel} < 1$) during the test (*22, 31, 32*). It is important to note that M_{rel} takes into account the total mass passing the sampling port because LAS sorption is an equilibrium process (i.e., reversible). Relative mass estimates for total LAS were less than unity at well M14 in the oxic zone (0.9) and in the transition zone (0.9 and 0.8 for wells M11 and M14, respectively) (Table 1) and decreased with increasing alkyl chain length and degree of external substitution for the individual LAS components (Tables 2 and 3). At well M11 in the oxic zone, relative masses for total LAS and the individual LAS components greater than unity, with the exception of the C_{13} 2- and 3-phenyl isomers, indicate that the observed mass of LAS at that well is at least as great as can be accounted for by the mass introduced. The underestimation of mass for the C_{13} 2- and 3-phenyl isomers is likely a result of termination of the sampling program before complete breakthrough occurred (Figure 4a). Values consistently greater than unity for both the total mixture and the individual components potentially indicate a positive analytical or sampling bias for LAS (*30, 32*). For example, it appears that the peak bromide concentration (see Figure 3a) may not have observed using the 1-day sampling interval, which could have positively biased relative LAS mass values.

At well M14 in the oxic zone and well M11 in the transition zone, most LAS components were conserved, with the exception of the C_{12} 2-phenyl isomer and all the C_{13} isomers (Tables 2 and 3). At well M14 in the transition zone, the relative masses of the C_{11}−C_{13} homologues all decreased, such that less than 50% of the injected C_{12} mass was detected and none of the C_{13} 2-phenyl isomer was detected (Table 3). Both sorption and biodegradation increase for the longer alkyl chain homologues and external isomers and, therefore, affect LAS mixture composition similarly, resulting in a mixture deficient in these components (*40, 41*). However, assuming that sorption is an equilibrium process, mass is not removed from the system. Because the possibility of analytical or sampling bias exists, it was not possible to discern the cause(s) of the apparent removal of LAS mass in the oxic and transition zones using relative mass alone. For this

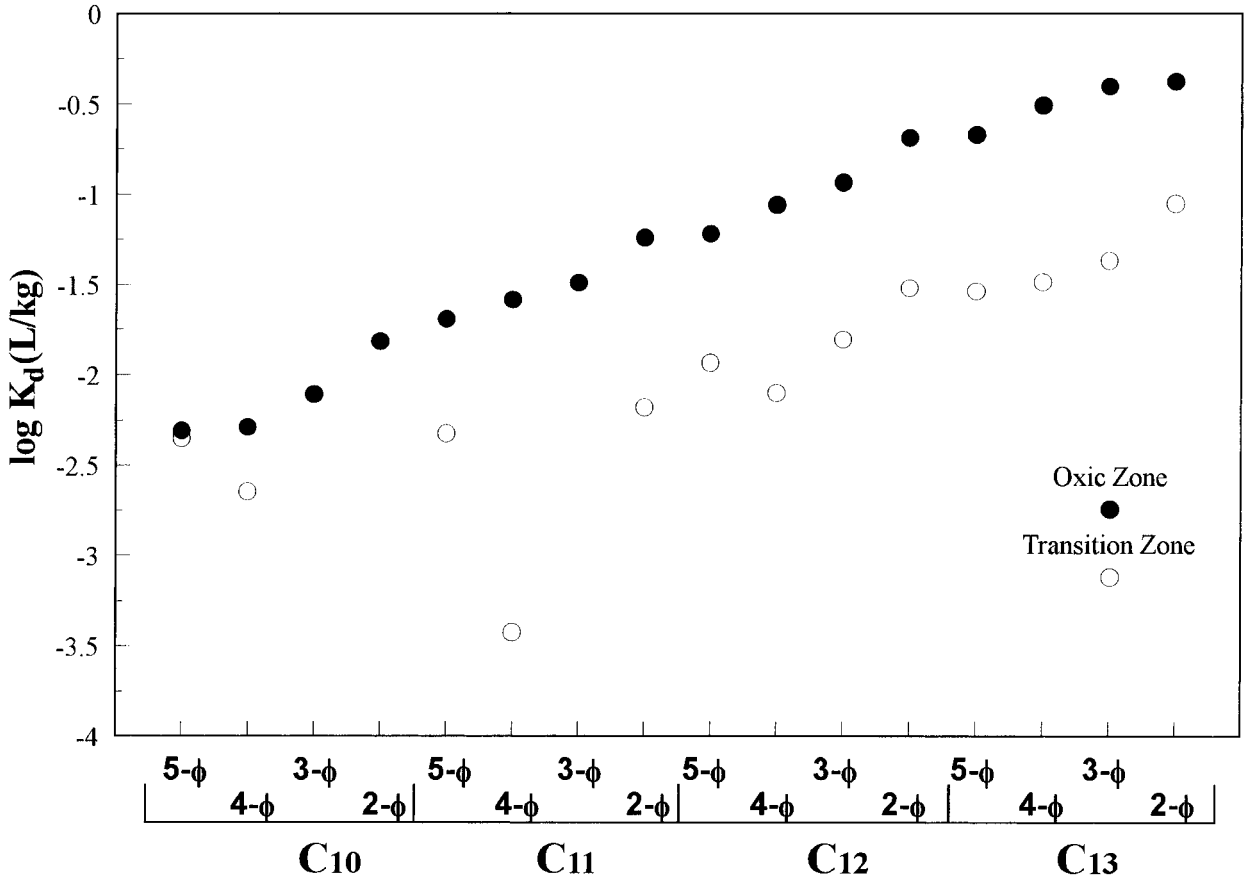

FIGURE 5. Sorption of LAS homologues and isomers to the oxic and transition zone sediments as a function of alkyl chain length and phenyl (ϕ) position.

purpose, it is useful to examine dissolved oxygen concentrations, the formation of LAS sulfophenylcarboxylate metabolites, and the response of indigenous microorganisms during the tracer tests.

In the oxic zone, no LAS metabolites were detected and no increase in free-living bacteria concentration over the background concentration was observed, suggesting that the M_{rel} values below unity observed for the C_{12} 2-phenyl and C_{13} isomers at well M14 may not have been due to biodegradation. Previous studies report more rapid biodegradation of the 2-phenyl isomers relative to internal isomers for all homologues in aerobic systems (*41, 42*). On the basis of this well-documented biodegradation pattern, one would expect to observe the loss of the 2-phenyl isomers of the C_{11} and possibly C_{10} homologues in an aerobic system that is actively degrading the C_{12} 2-phenyl and C_{13} isomers. However, this pattern was not observed in the oxic zone (Table 2), yet it was observed in the transition zone at both wells (Table 3). The absence of metabolites in the oxic zone could be interpreted as mineralization. However, LAS sulfophenylcarboxylate metabolites have been detected in aerobic LAS laboratory biodegradation studies (*43*−*45*), sewage effluent (*27, 46*), receiving surface waters (*27*), and suboxic sewage-contaminated groundwater (*46*), which indicates that aerobic conditions such as those that exist in the oxic zone do not necessarily result in the complete mineralization of all LAS metabolites. Therefore, the absence of metabolites together with the lack of the characteristic biodegradation pattern suggest that biodegradation did not occur in the oxic zone. Although we cannot completely dismiss biodegradation, the lack of substantiating evidence indicates that there may be another explanation such as negative analytical bias. One explanation for the relative mass values below unity for the C_{12} 2-phenyl and C_{13} isomers may be negatively biased zeroeth moments resulting from aqueous phase concentrations that decrease below detection in the tail of the breakthrough curve as a result of sorption of these more hydrophobic species. It should be noted that the C_{13} homologue constitutes less than 10% of the total LAS mixture so that its aqueous phase concentration is the first to decrease below detection.

In contrast, the dissolved oxygen concentrations in the transition zone declined rapidly from 0.7 to ~0.1 mg/L at well M11 by day 17 (Figure 6a) and from 1.0 to ~0.1 mg/L at well M14 on day 28, just after arrival of the LAS peak. In both wells, dissolved oxygen concentrations remained at ~0.1 mg/L throughout the remainder of the test, which suggests oxygen consumption due to LAS biodegradation. The initial step in LAS biodegradation, ω-oxidation of the terminal methyl group to form the corresponding sulfophenylcarboxylate metabolite requires O_2 whereas subsequent β-oxidation may proceed in the absence of O_2 using water as the electron acceptor (*41, 42*). Coincident with the decline in dissolved oxygen concentration was the appearance of LAS metabolites in wells M11 (Figure 6a) and M14. The total mass of metabolites was found to be nearly equal to that of the mass of total LAS lost, based on the area under the curves for LAS and metabolites, normalized to that of bromide. For example, LAS metabolites accounted for 78% and 86% of the missing LAS mass at M11 and M14, respectively, so that together the LAS mass remaining and LAS metabolites formed accounted for 98% and 97% of the total LAS mass injected. Because the sulfophenylcarboxylate metabolites accounted for the missing LAS mass, it is clear that ω-oxidation of LAS occurred during the test. Therefore, the ~1 mg/L groundwater dissolved oxygen concentration was sufficient for 20% of the LAS mixture to undergo ω-oxidation. Furthermore, the observed metabolites were stable over the duration of the tracer test, indicating that complete mineralization of

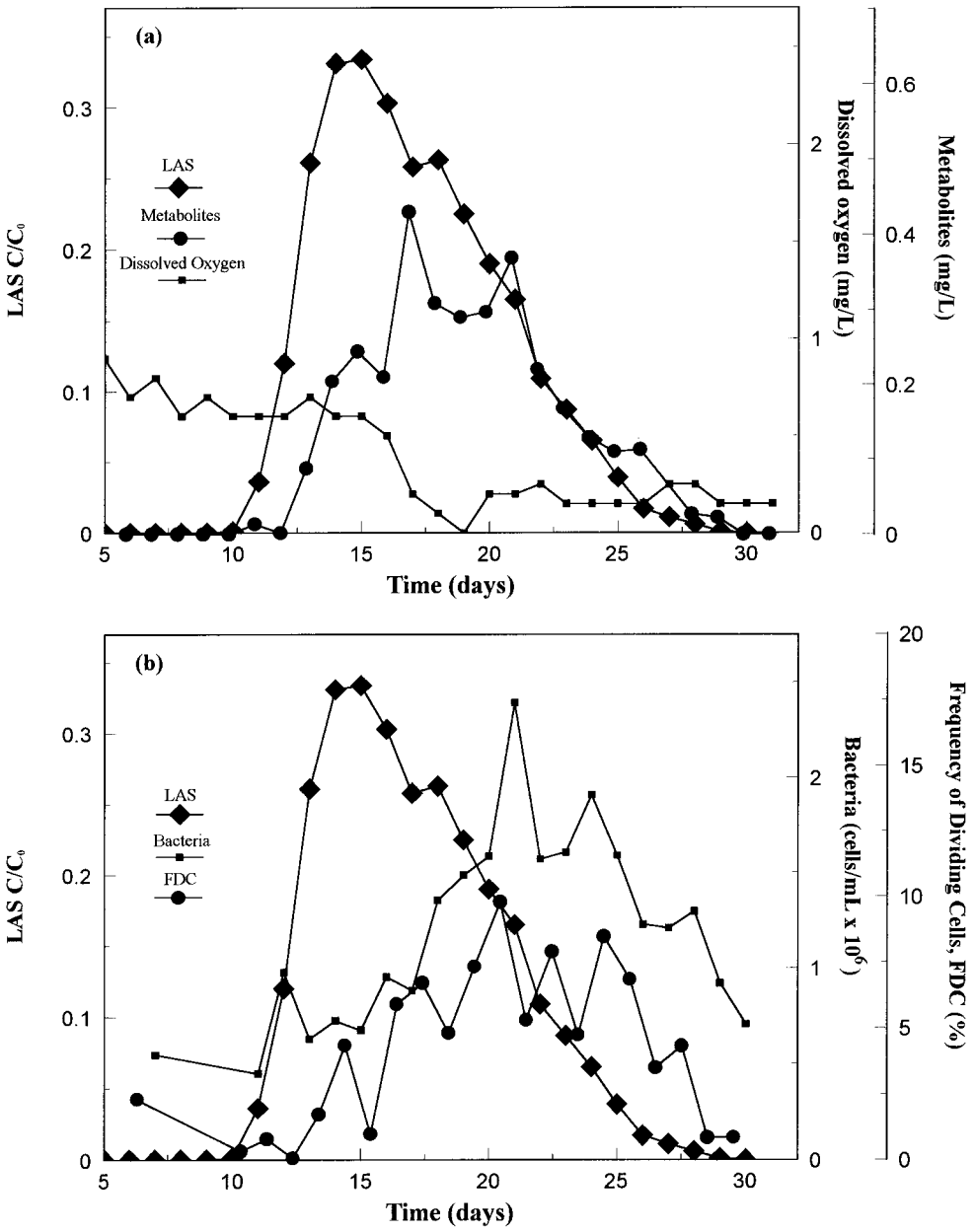

FIGURE 6. Concentration profiles at well M11 in the transition zone of (a) the total LAS mixture, LAS metabolites, and dissolved oxygen concentrations and (b) the total LAS mixture, total number of free-living bacteria, and frequency of dividing cells.

the metabolites did not occur under the conditions of the test. In fact, the metabolites formed during the test are similar to those in the background groundwater at the site (*46*).

An approximately 5-fold increase in the number of free-living bacteria over the background concentration was observed in samples collected from the transition zone at wells M11 (Figure 6b) and M14. However, it should be noted that the numbers of free-living bacteria represent only a small fraction of the total microbial population in the subsurface at this site (*28, 47*). Qualitative changes also were observed in the morphology of the free-living bacteria. For example, free-living bacteria cells at peak LAS concentrations were more elongated and the brightness and size (0.2−2 μm) of the stained bacteria was greater than that of bacteria in background samples (0.2−0.5 μm). Frequency of dividing cells (FDC), attained maximum values of 10% and 16% FDC at wells M11 (Figure 6b) and M14, respectively, which suggests that bacteria growth may have occurred during the test.

It is not clear whether the increase in free-living bacteria is due to growth or due to the detachment and mobilization of bacteria by LAS or a combination of the two processes. No increase in cell numbers was observed in the oxic zone whereas a 3-fold increase was observed in the suboxic zone (*17*). We hypothesize that the indigenous bacteria populations in the sewage-contaminated suboxic and transition zones are acclimated to LAS and LAS-related compounds because these compounds are present at low levels in the groundwater. Because biodegradation did not occur under the oxygen-limited conditions of the suboxic zone test despite the presence of potentially acclimated bacteria, the observed increase in cell numbers may have been due to detachment. Likewise, the long-term exposure to LAS and related compounds in the transition zone make detachment and mobilization of sediment-bound bacteria in response to the LAS one possible explanation for the observed increase in bacteria numbers in that zone. In contrast, indigenous bacteria in the uncontaminated oxic zone have had no prior exposure to either sewage-contaminated groundwater or to LAS, which may account for the absence of detachment and mobilization in the oxic zone. No information was collected

TABLE 4. Calculated First-Order Rate Constants for Biodegradation of Total LAS and Individual LAS Components at Wells M11 and M14 in the Transition Zone

	monitoring well M11	monitoring well M14
LAS component	k_1 (day^{-1})	k_1 (day^{-1})
C_{10} 2-ϕ	0.002	0.004
C_{10} 3-ϕ	0.003	0.004
C_{10} 4-ϕ		0.002
C_{10} 5-ϕ		
C_{11} 2-ϕ	0.004	0.009
C_{11} 3-ϕ	0.006	0.009
C_{11} 4-ϕ	0.002	0.005
C_{11} 5-ϕ		
C_{12} 2-ϕ	0.015	0.031
C_{12} 3-ϕ	0.010	0.016
C_{12} 4-ϕ	0.010	0.016
C_{12} 5-ϕ		0.002
C_{13} 2-ϕ	0.085	nd
C_{13} 3-ϕ	0.021	0.048
C_{13} 4-ϕ	0.027	0.057
C_{13} 5-ϕ	0.008	0.028

[a] nd, not detected.

on either the sediment-bound bacteria, which represents the majority of the biomass in the system, or on the numbers of protozoa, which graze on indigenous bacteria. This lack of information limits our ability to more fully interpret the microbial response to the LAS pulse during the tracer test.

Previous studies of LAS biodegradation in subsurface sediments have found LAS biodegradation rates to follow first-order kinetics (*8, 48, 49*), which assumes that no microbial growth occurs. In this study it is evident that LAS is being biodegraded but it is not clear if the bacterial population is increased as a result of growth. Assuming that the loss in LAS mass in the transition zone is due entirely to biodegradation and that the biodegradation obeys first-order kinetics, it is possible to estimate first-order rate constants, k (day^{-1}), according to

$$\ln M_{rel} = -k\bar{t} \quad (1)$$

Rates ranged from 0.002 to 0.085 day^{-1} and were greater for the longer alkyl chain homologues and external isomers (Table 4). In contrast, previous studies reported that biodegradation rates did not vary significantly for the different LAS homologues and isomers with estimated rates ranging from 0.35 to 0.8 day^{-1} for river water and sediments (*3, 8, 48, 49*) and from 0.03 to 0.06 day^{-1} for subsurface sediments (*3, 8, 49*). These latter results for subsurface sediments are comparable to estimated rates in this study, however, only for the more biodegradable C_{12} 2-phenyl and C_{13} isomers. In general, the rates for most of the LAS components were <0.02 day^{-1} (Table 4) with overall rates of 0.005−0.009 day^{-1} observed for the total LAS mixture at wells M11 and M14, respectively, indicating that LAS biodegradation proceeds at a slower rate under in situ low-oxygen conditions than is predicted by laboratory microcosms.

Implications. The information gained from these tracer tests indicate that sorption and biodegradation affect the fate and transport of surfactants present at low concentrations in groundwater. Preferential sorption and biodegradation of the longer alkyl chain homologues and external isomers observed during the tests result in aqueous phase mixtures enriched in the more hydrophilic, more mobile, and biologically resistant components, which also have lower aqueous toxicities (*50, 51*). The enrichment of LAS mixtures in the shorter alkyl chain homologues and internal isomers that was observed in this study is consistent with previous observations made by Field et al. (*4, 46*). They reported the occurrence and distribution of LAS and its metabolites in groundwater at the Cape Cod site and hypothesized that LAS was readily transported in the low-organic carbon aquifer sediments and underwent limited or negligible biodegradation due to oxygen limitations.

Previous studies report LAS to be readily biodegraded in various environments; however, they generally are not conducted under oxygen-limited conditions that exist in some contaminated groundwaters. In this study, partial removal of LAS and the appearance of LAS metabolites in the transition zone demonstrate that biodegradation occurred and at the same time reduced dissolved oxygen concentrations to levels comparable to those in the suboxic zone in which no biodegradation was observed. This suggests that, once groundwater concentrations of dissolved oxygen have been depleted with no additional input of oxygen, LAS and its metabolites likely will persist. The observation of no LAS biodegradation in the oxic zone indicates that aerobic conditions are not the only prerequisite for LAS biodegradation.

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